

Unveiling the *Penta*-Silicene nature of perfectly aligned single and double strand Si-nanoribbons on Ag(110)

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From the simplest cyclopentane ring and its numerous organic derivatives to their common appearance in extended geometries such as edges or defects in graphene, pentagons are frequently encountered motifs in carbon related systems. Even a *penta*-graphene Cairo-type two dimensional structure has been proposed as a purely pentagonal C allotrope with outstanding properties competing with those of graphene [1]. Conversely, pentagonal Si motifs are hardly found in nature. Despite the large effort devoted to design Si-based structures analogous to those of carbon, the existence of Si pentagonal rings has only been reported in complex clathrate bulk phases [2]. Several theoretical studies have hypothesized stable Si pentagonal structures either in the form of one-dimensional (1D) nanotubes [3, 4] or at the reconstructed edges of *silicene* nanoribbons [5, 6] or even as hydrogenated *penta-silicene* [7] or highly corrugated fivefold coordinated *siliceneet* [8] 2D sheets, the latter recognized as a topological insulator [9]. However, to date none of them have yet been synthesized. In the present work we unveil, via extended Density functional theory (DFT) [10] calculations and Scanning tunneling microscopy (STM) simulations [11, 12], the atomic structure of 1D Si nano-ribbons grown on the Ag(110) surface. Our analysis reveals that this system constitutes the first experimental evidence of a silicon phase solely comprising pentagonal rings.

Since their discovery in 2005 [13] the atomic structure of Si nano-ribbons (NRs) on Ag(110) has remained elusive and strongly disputed [13–21]. Figure 1 presents a summary of Si NRs measured with STM. The structures were obtained after Si sublimation onto a clean Ag(110) surface at RT. Panels (a) and (b) correspond to a low Si coverage image with an isolated *nano-dot* structure and a *single strand* NR (SNR) 0.8 nm wide running along the $[1\bar{1}0]$ direction with a $2\times$ periodicity. The SNR topography consists of alternating protrusions at each side

of the strand with a glide plane. At higher coverages and after a mild annealing, a dense and highly ordered phase is formed (panel (c)) consisting of *double strand* NRs (DNRs) with a $5\times$ periodicity along the $[001]$ direction again exhibiting a glide plane along the center of each DNR. The images are in perfect accord with previous works [13, 15, 20, 21]. Further key information on the system is provided by the high-resolution Si-2*p* core level photoemission spectrum for the DNRs displayed in Figure 1(d) –that for the SNRs is almost identical [22]. The spectrum can be accurately fitted with only two (spin-orbit split) components having an intensity ratio of roughly 2:1. Furthermore, previous Angular Resolved Photoemission (ARPES) experiments [23] assigned the larger and smaller components to subsurface Si_s and surface Si_{ad} atoms, respectively, indicating that the NRs comprise two different types of Si atoms, with twice as many Si_s as Si_{ad} .

We first focus on the *nano-dot* shown in Fig. 1(a), as it may be regarded as the precursor structure for the formation of the extended NRs. The *nano-dot* exhibits a local *pmm* symmetry with two bright protrusions aligned along the $[001]$ direction, each of them having two adjacent dimmer features along the $[1\bar{1}0]$ direction. After considering a large variety of trial models (see 'Extended Data' Fig 10) we found that only one, shown in Figure 2, correctly reproduces the experimental image both in terms of aspect and overall corrugation. It consists of a ten atom Si cluster located in a double silver vacancy generated by removing two adjacent top row silver atoms. There are four symmetry equivalent Si_s atoms residing deeper in the vacancy, two Si_{ad}^1 in the middle which lean towards short silver bridge sites and four outer Si_{ad}^2 residing at long bridge sites. The formers lie 0.8 Å above the top Ag atoms and are not resolved in the STM image, while the Si_{ad}^1 and Si_{ad}^2 protrude out of the surface by 1.4 and 1.1 Å thus leading to the six bump structure in the simulated image with the Si_{ad}^1 at the center appearing brighter. Therefore, although the *nano-dot* shows marked differences with respect to the extended NRs, its structure already accounts for the presence of two dis-

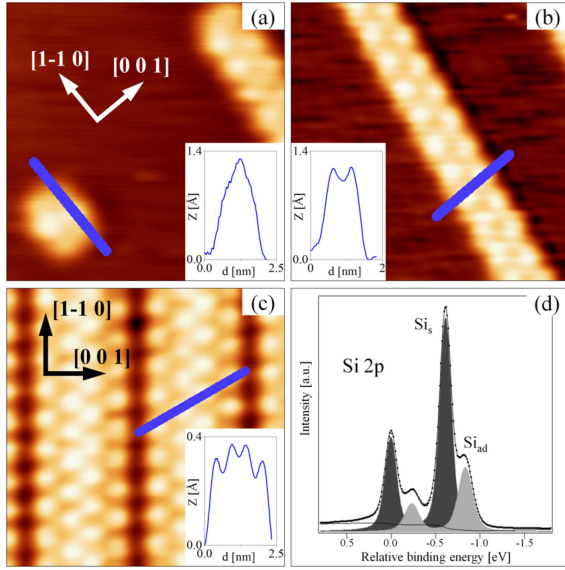


FIG. 1. (Color online) $5.3 \times 5.3 \text{ nm}^2$ STM images of Si nanostructures on Ag(110). (a) a Si *nano-dot*, (b) a Si SNR and (c) an extended Si DNR phase. The insets show profiles along the solid lines passing over the maxima in the images. Tunneling parameters: (a) -1.5 V, 2.4 nA, (b) -1.8 V, 1.2 nA and (c) 1.3 V, 1.1 nA. (d) Si-2p core level photoemission spectra recorded at normal emission and at 135.8 eV photon energy for the Si DNRs structure.

tinct types of Si atoms at the surface (Si_s and Si_{ad}). Furthermore, it reveals the tendency of the Ag(110) surface upon Si adsorption to remove top row silver atoms (i.e. the initial stage in the creation of a missing row (MR)) and incorporate Si nanostructures in the troughs.

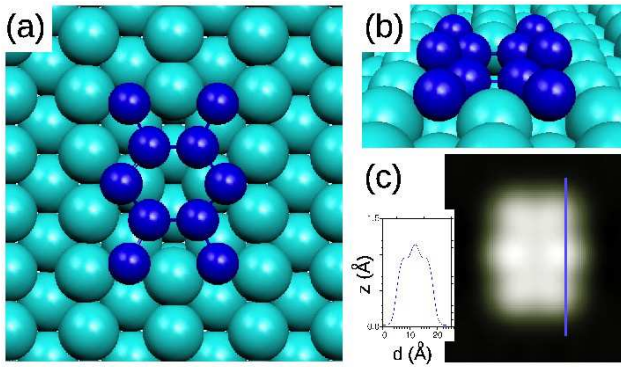


FIG. 2. (a-b) Top and perspective views of the *nano-dot* structure. (c) Simulated STM topographic image and line profile along the solid line.

Inspired by the *nano-dot* Ag di-vacancy structure and by recent grazing incidence X-ray diffraction (XRD) measurements [24] pointing towards the existence of a MR reconstruction along the $[1\bar{1}0]$ direction of the Ag surface, we considered several trial structures for the SNRs by placing Si atoms in the MR troughs (Si_s) and next

adding further adatoms (Si_{ad}) on top, while maintaining a 2:1 concentration ratio between the two. Figures 3(a-b) show top and side views of the optimized geometry for the SNRs after testing several trial models (see 'Extended Data' Fig. 8). It involves a MR and six Si atoms per cell. The new paradigm is the arrangement of the Si atoms into pentagonal rings running along the MR and alternating their orientation (we denote it as the P-MR model). Despite no symmetry restriction was imposed, the relaxed P-MR SNR belongs to the *cm* group presenting two mirror planes plus an additional glide plane along the MR troughs (see 'Extended Data' Fig. 6 for a detailed description). Apart from a considerable buckling of 0.7 \AA between the lower Si atoms residing in the MR troughs (Si_s) and the higher ones (Si_{ad}) leaning towards short bridge sites at the top silver row, the pentagonal ring may be considered as rather perfect, with a very small dispersion in the Si-Si distances ($2.35 - 2.37 \text{ \AA}$) and bond angles ranging between $92^\circ - 117^\circ$; that is, all close to the 108° in a regular pentagon. The associated STM image and line profile, panel (d), show (symmetry) equivalent protrusions 1.3 \AA high at each side of the strand, in perfect agreement with the experimental image. Still, since different models may yield similar STM images, a more conclusive gauge to discriminate among them is to examine their relative formation energies. In this respect, the energetic stability of the P-MR structure is far better ($\sim 0.1 \text{ eV/Si}$) than all other SNR models considered (see section 'Methods' and 'Extended Data' Fig. 9).

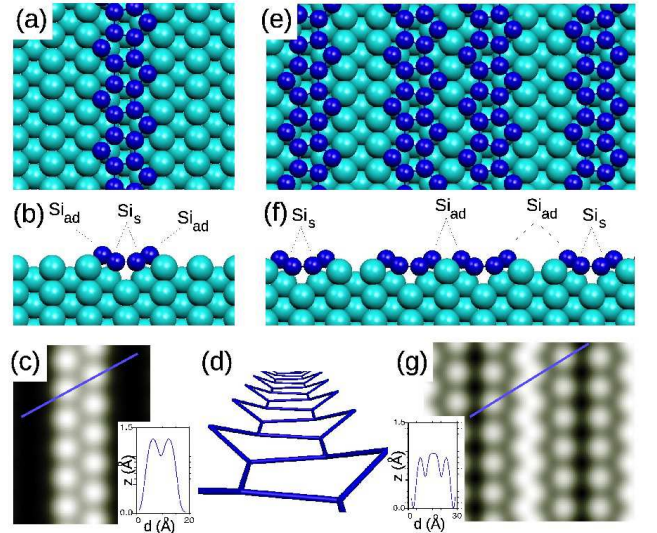


FIG. 3. Optimized geometry of the pentagonal missing row (P-MR) model (a-c) Top, side and simulated topographic STM image for the SNR phase. (d) Perspective view of a penta-silicene strand without the silver surface. (e-g) Top, side and simulated topographic STM image for the DNR array. Insets in (c) and (g) show line profiles along the blue lines indicated in the topographic maps. All STM simulations employed a sharp Si ended tip apex and set points $V = -0.2 \text{ V}$ and $I = 1 \text{ nA}$.

Within the pentagonal model the DNR structure may be naturally generated by placing two SNRs within a $c(10 \times 2)$ cell. However, since the P-MR SNRs are chiral, adjacent pentagonal rings may be placed with the same or with different handedness, leading to two possible arrangements among the enantiomers. Figures 3(e-g) display the optimized geometry and simulated STM topography for the most stable (by 0.03 eV/Si) P-MR DNR configuration. The pentagonal structure in each NR is essentially preserved, the main difference with respect to the SNRs being the loss of the glide plane along the MR troughs replaced by a new one along the top silver row between adjacent SNRs. There is a slight repulsion between the NRs which shifts them away from each other by around 0.2 Å. As a result, the Si_{ad} at the outer edges of the DNR end up lying 0.07 Å higher than the inner ones making the alternating pentagons along each strand not strictly equivalent anymore. In the simulated STM image the outer maxima appear dimmer than the inner ones by 0.1 Å, which adopt a zig-zag aspect. The inversion in their relative corrugations is due to the proximity between the inner Si adatoms (~ 4 Å) compared to the almost 6 Å distance between the inner and outer ones, so that the bumps of the formers overlap and lead to brighter maxima. All these features are in accordance with the experimental profiles shown in Fig. 1(c). In fact, the P-MR DNR structure is the most stable among all other NR models considered for a wide range of Si chemical potentials ranging from Si-poor to -rich conditions (see 'Extended Data' Fig. 9).

Figure 4 presents a summary of the electronic properties of the P-MR structure. Panel (a) shows an isosurface of the total electronic density for the SNRs. The Si_s atoms in the pentagonal rings are clearly linked through an sp^2 type bonding (three bonds each) while the Si_{ad} , due to the buckling, show a distorted sp^3 type tetrahedral arrangement making bonds with two Si_s as well as with the adjacent short bridge silver atoms in the top row. Panel (b) displays ARPES spectra for the SNR and DNR phases. Both energy distribution curves reveal Si-related peaks previously attributed to *quantum well states* (QWS) originating from the lateral confinement within the NRs.

For the SNRs three states are observed at -1.0, -2.4 and -3.1 eV binding energy (BE), while for the DNRs one further peak is identified at -1.4 eV. The computed (semi-infinite) surface band structures projected on the Si pentagons (blue) and the silver MR surface (red) are superimposed in panels (c) and (d) for the SNRs and DNRs, respectively. Overall, within the expected DFT accuracy and experimental resolution, the maps satisfactorily reproduce the experimental spectra. At Γ the SNRs present two sharp intense Si bands below the Fermi level (S1 and S3) and faint (broader) features arising from two almost degenerate bands (S4 and S5) and a dimmer state (S2). As expected, they are almost flat along $\Gamma - X$

while along $\Gamma - Y$ they present an appreciable dispersion and finally merge into two degenerate states at the high symmetry Y point. The orbital character of the S2-S5 bands is mainly p_{xy} and may thus be assigned to localized sp^2 planar bonds. Conversely, band S1 is fully dominated by the $\text{Si}_s - p_z$ states (π -band) and shows a strong downward dispersion along $\Gamma - Y$ due to hybridization with the metal sp bands. Similarly, faint dispersive bands of mainly p_z character hybridizing with the metal appear in the empty states region. The electronic structure for the DNRs is similar to that of the SNRs, except that the number of Si bands is doubled and most of them become split and shifted due to the interaction between adjacent SNRs. Noteworthy is the appearance of an electron pocket (EP) at Γ associated to a parabolic $\text{Si}-p_z$ band with onset at -0.5 eV.

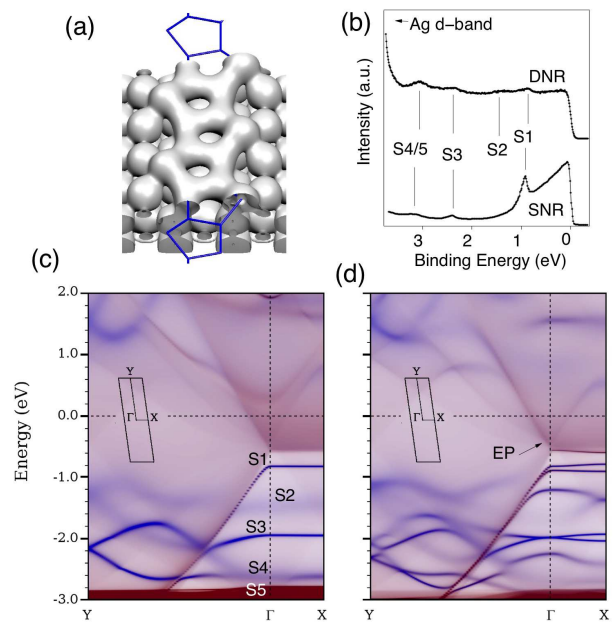


FIG. 4. Electronic structure of the P-MR model. (a) Charge density isosurface for the SNRs with blue sticks indicating the Si pentagons. (b) Energy distribution curves around the X point for the SNRs acquired at 78 eV photon energy (adapted from Ref [25]) and for the DNRs at 75 eV. (c-d) PDOS(\vec{k}, E) projected on the Si (blue) and Ag (red) atoms along the $Y - \Gamma - X$ k -path (see insets) for the SNRs and DNRs, respectively.

To conclude, we have solved the long debated structure of silicon nano-ribbons on Ag(110), finding an unprecedented 1D *penta-silicene* phase which consists of adjacent inverted pentagons stabilized within the MR troughs. The model is in accordance with most of previous experimental results for this system: it involves a MR reconstruction as deduced from XRD [24], comprises two types of Si atoms with a ratio 2:1 between the Si_s and Si_{ad} concentrations as seen by photoemission, accurately matches the STM topographs also explaining dislocation

defects between NRs (see 'Extended Data' Fig. 7) and accounts for the QWS measured by ARPES. We have also determined the quasi-hexagonal geometry of a Si *nanodot* inside a silver-divacancy. This precursor structure for the NRs can be considered as the limiting process for expelling surface Ag atoms in order to create a missing row along which the Si pentagons can develop. We are convinced that the discovery of this novel silicon allotrope will promote the synthesis of analogous exotic Si phases on alternative templates with promising properties [8].

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METHODS

Experimental

For both types of prepared structures (isolated Si SNRs or ordered DNRs), the same procedure has been used for sample preparation: i.e. the Ag(110) substrate was cleaned in the Ultra-high vacuum (UHV) chambers (base pressure: 9×10^{-11} mbar) by repeated sputtering of Ar^+ ions and subsequent annealing of the substrate at 750 K, while keeping the pressure below 3×10^{-10} mbar during heating. Si was evaporated at a rate of 0.03 ML/min from a silicon source in order to form the NRs. The Ag substrate was kept at room temperature RT to form the isolated SNR 0.8 nm wide, while a mild heating of the Ag substrate at 443 K allows the formation of an ordered grating DNR 1.6 nm wide [1].

STM measurements were done with a home-made variable temperature UHV STM [2]. All STM data were measured and processed with the WSxM software [3]. High-Resolution Photoelectron Spectroscopy (HRPES) experiments of the shallow Si-2*p* core-levels and of the valence states, were carried out to probe, comparatively, the structure and the electronic properties of those nanostructures. The ARPES experiments were carried out at the I511 beamline of the Swedish Synchrotron Facility MAX-LAB in Sweden. The end station is equipped with a Scienta R4000 electron spectrometer rotatable around the propagation direction of the synchrotron light. It also houses low energy electron diffraction (LEED) and sputter cleaning set-ups. Further details on the beam line are given in Ref. [4]. In all the photoemission spectra the binding energy is referenced to the Fermi level. The total experimental resolution for core level and valence band (VB) spectra were 30 meV ($h\nu=135.8$ eV for Si-2*p*) and 20 meV ($h\nu=75$ eV for the VB), respectively. A least-square fitting procedure was used to analyze the core-levels, with two doublets, each with a spin-orbit splitting of 610 ± 5 meV and a branching ratio of 0.42. The Si-2*p* core level collected at normal emission is dominated by the Si_s component. Its full width at half maximum (FWHM) is only 68 meV while the energy difference be-

tween the two Si_s and Si_{ad} components is 0.22 eV.

Theory

All calculations have been carried out at the *ab initio* level within the Density Functional Theory (DFT) employing the SIESTA-GREEN package [5, 6]. For the exchange-correlation (XC) interaction we considered both the Local Density [7] (LDA) as well as the Generalized Gradient [8] (GGA) approximations. The atomic orbital (AO) basis set consisted of Double-Zeta Polarized (DZP) numerical orbitals strictly localized after setting a confinement energy of 100 meV in the basis set generation process. Real space three-center integrals were computed over 3D-grids with a resolution equivalent to a 700 Rydbergs mesh cut-off. Brillouin zone (BZ) integration was performed over *k*-supercells of around (20×28) relative to the Ag-(1×1) lattice while the temperature *kT* in the Fermi-Dirac distribution was set to 100 meV.

All considered Si-NR-Ag(110) structures were relaxed employing two-dimensional periodic slabs involving nine metal layers with the NR adsorbed at the upper side of the slab. A $c(10 \times 2)$ supercell was employed for both the SNR and DNR structures. In all cases, the Si atoms and the first three metallic layers were allowed to relax until forces were below 0.02 eV/Å while the rest of silver layers were held fixed to their bulk positions (for which we used our LDA (GGA) optimized lattice constant of 4.07 Å (4.15 Å), slightly smaller (larger) than the 4.09 Å experimental value).

For the *nano-dot* calculations, and given that a larger unit cell is required to simulate its isolated geometry, the atomic relaxations of all the trial models (see Fig. 10) were carried out for (4×5) or (4×6) supercells. STM topographic images were next computed for all relaxed structures after recomputing the slab Hamiltonians with highly-extended AOs for the surface atoms. Once the correct structure was identified (see Fig. 10), we further optimized it increasing the unit cell to a (6×10) to remove any overlaps between image cells (see Fig. 2 in the main text).

Band structure– In order to examine the surface band dispersion we computed *k*-resolved surface projected density of states PDOS(*k*, *E*) maps in a semi-infinite geometry. To this end we stacked the Si-NR and first metallic layers on top of an Ag(110) bulk-like semi-infinite block via Green's functions matching techniques following the prescription detailed elsewhere [9, 10]. For this step we recomputed the slab's Hamiltonian employing highly extended orbitals (confinement energy of just 10-20 meV) for the Si and Ag surface atoms in the top two layers (this way the spatial extension of the electronic density in the vacuum region is largely extended and the calculation becomes more accurate).

STM simulations– For the STM simulations we modeled the tip as an Ag(111) semi-infinite block with a one-atom terminated pyramid made of ten Si atoms stacked below acting as the apex (see Figure 5). Test calcula-

tions employing other tips (e.g. clean Ag or clean W) did not yield any significant changes. Highly extended orbitals were also employed to describe the apex atoms thus reproducing better the expected exponential decay of the current with the tip-sample normal distance z_{tip} . Tip-sample AO interactions were computed at the DFT level employing a slab including the Si NR on top of three silver layers as well as the Si tip apex. The interactions (Hamiltonian matrix elements) were stored for different relative tip-surface positions and next fitted to obtain Slater-Koster parameters that allow a fast and accurate evaluation of these interactions for any tip-sample relative position [10]. Our Green's function based formalism to simulate STM images includes only the elastic contribution to the current and assumes just one single tunneling process across the STM interface; it has been extensively described in previous works [6, 10]. Here we employed an imaginary part of the energy of 20 meV which also corresponds to the resolution used in the energy grid when integrating the transmission coefficient over the bias window. We further assumed the so called wide band limit (WBL) at the tip [10] in order to alleviate the computational cost and remove undesired tip electronic features. The images were computed at different biases between -2 to +2 V scanning the entire unit cell with a lateral resolution of 0.4 Å always assuming a fixed current of 1 nA. Nevertheless, the aspect of the images hardly changed with the bias, in accordance with most experimental results.

Energetics—To establish the energetic hierarchy among different Si NR structures we first computed their adsorption energies (per Si atom), E_{ads} , via the simple expression:

$$E_{ads} = (E_{tot}(N_{Ag}, N_{Si}) - E_{surf}(N_{Ag}) - N_{Si}E_{Si}^0) / N_{Si} \quad (1)$$

where $N_{Si/Ag}$ are the number of Si and Ag atoms in the slab containing the NR and the Ag(110) surface, $E_{tot}(N_{Ag}, N_{Si})$ refers to its total energy, $E_{surf}(N_{Ag})$ the energy of the clean Ag surface without the NRs (but including any MRs) and E_{Si}^0 the energy of an isolated Si atom. In the low temperature limit eq. (1) allows to discriminate between structures with the same number of silver and Si atoms.

However, a more correct approach to compare the NR's stabilities between structures with different Si and Ag concentrations is to compute their formation energies, γ , as a function of the Si and Ag chemical potentials, $\mu_{Si/Ag}$. To this end, we employ the standard low temperature expression for the grand-canonical thermodynamic potential [11]:

$$\Omega(\mu_{Si}, \mu_{Ag}) = E_{tot}(N_{Si}, N_{Ag}) - N_{Si}\mu_{Si} - N_{Ag}\mu_{Ag} \quad (2)$$

The chemical potentials may be obtained via $\mu_{Ag/Si} = E_{Ag/Si}^{ref} - E_{Ag/Si}^0$, where E^0 corresponds to the total energy of the isolated atom and E^{ref} to that of a reference

structure acting as a reservoir of Ag or Si atoms. Here we use the bulk *fcc* phase for silver ($\mu_{Ag}^{LDA} = -4.67$ eV and $\mu_{Ag}^{GGA} = -3.60$ eV), while that of Si is considered as a parameter (see below). The NR's formation energy, normalized to the Ag(110)-(1 × 1) surface unit cell area, then takes the form:

$$\gamma = \frac{1}{N} [E_{tot}(N_{Si}, N_{Ag}) - N_{Ag}E_{Ag}^{ref} - N_{Si}\mu_{Si}] - \gamma_{Ag}^{sb} \quad (3)$$

with $N = 10$ because the same $c(10 \times 2)$ was used for all NR structures and γ_{Ag}^{sb} accounts for the formation energy of the unrelaxed surface at the bottom of the slab, which was obtained according to: $\gamma_{Ag}^{sb} = \frac{1}{2}[E_{1 \times 1}(N_{Ag}) - N_{Ag}E_{Ag}^{ref}]$ with $E_{1 \times 1}(N_{Ag})$ giving the total energy of an unrelaxed nine layers thick Ag(110)-(1 × 1) slab.

We follow the standard procedure of treating the Si chemical potential as a parameter in eq. (3) and plot the formation energies for each structure as a function of μ_{Si} in Figures 9(a) and (b) for the LDA and GGA derived energies, respectively. However, since a reference structure for the Si reservoir is not available (and hence the absolute value of μ_{Si} is unknown) we plot the formation energies as a function of a chemical potential shift, $\Delta\mu_{Si}$, whose origin is placed at the first crossing between the formation energy of the clean Ag(110) and that of any of the NRs (in our case it corresponds to the P-MR DNR structure). Within this somewhat arbitrary choice, small or negative values of $\Delta\mu_{Si}$ would correspond to Si poor conditions, while large positive values to Si rich conditions.

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Si₁₀-Ag(111) tip

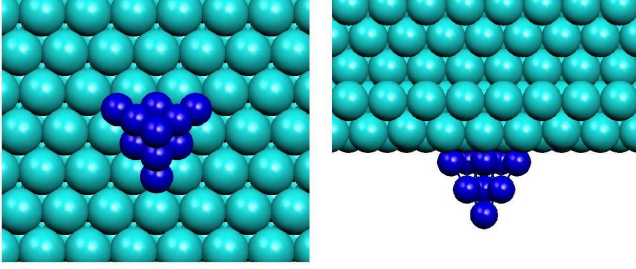


FIG. 5. **Si₁₀-Ag(111) tip**: Bottom and side views of the Ag(111) tip terminated in a 10 Si atom pyramid employed for all STM simulations.

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	atom	z (Å)	d_{Si-Ag} (Å)
SNR	Si _{ad}	1.42	2.56 (×2), 2.80
	Si _s	0.68	2.58, 2.74
DNR	Si _{ad} ¹	1.44	2.55 (×2), 2.87
	Si _{ad} ²	1.38	2.56 (×2), 2.78
	Si _s ¹	0.68	2.58, 2.73
	Si _s ²	0.58	2.58, 2.76

TABLE I. **Details of the P-MR/Ag(110) geometry**: Relative vertical distances (z) with respect to the average top-most Ag layer and bond distances to the first silver nearest neighbor (d_{Si-Ag}) for each of the symmetry inequivalent atoms in the SNR and DNR structures –see Fig. 6 for further details.

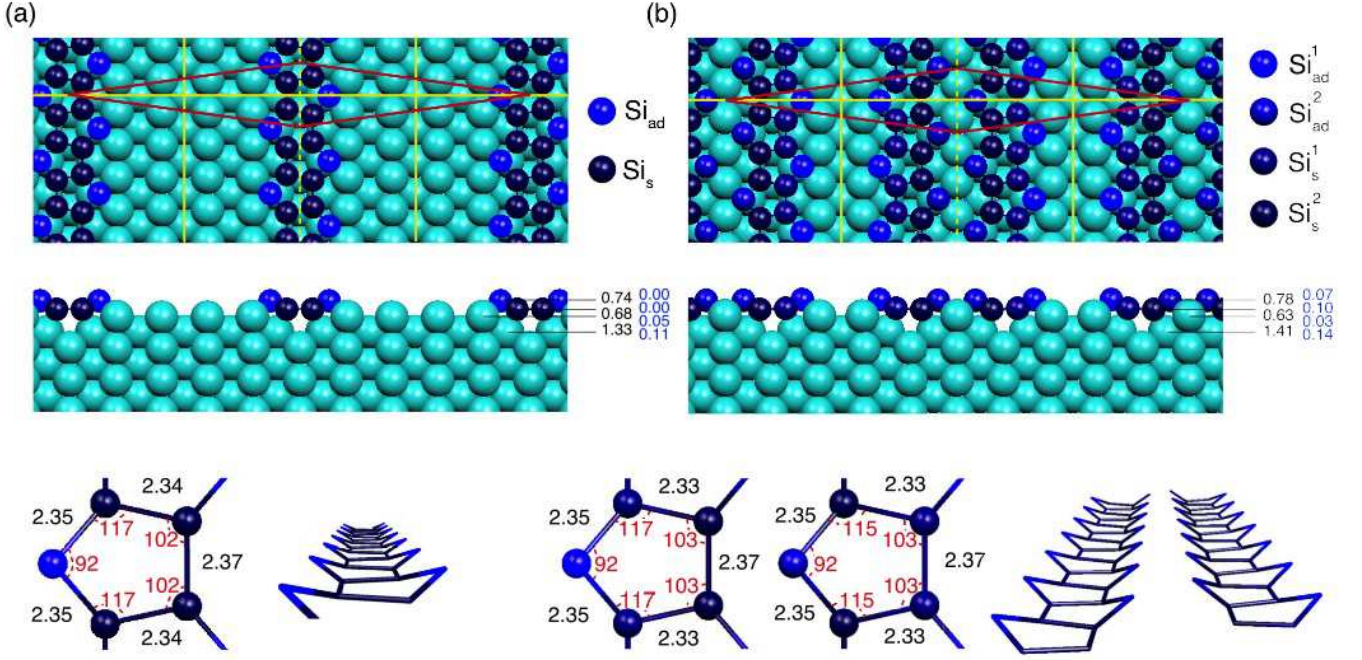


FIG. 6. **Geometry of the P-MR model:** P-MR/Ag(110) optimized structures for the Si SNRs (a) and the DNRs (b). The Si atoms have been colored according to the symmetry inequivalent group they belong (see legends). Top panels: top views with the $c(10 \times 2)$ supercell indicated by the dark rhombus while green thick and dashed lines correspond to mirror and glide symmetry planes, respectively. The overall symmetry for both models is $cm\bar{m}$. Middle panels: side views with the normal averaged distances between the Si_{ad} , Si_{s} and the two first silver layers indicated by black numbers, and the buckling within each group of atoms given by blue numbers (all distances in Å). Bottom panels: Zoom in of the pentagonal rings including the Si-Si bond distances (in Å) and bond angles (in red), and perspective views of the 1D pentagonal structures. In Table I we additionally provide the relative z -coordinate of the Si atoms and their nearest neighbor distances to the metal atoms. In the DNR phase the loss of the local glide plane within each NR makes the two Si_{ad} at each side of the pentagonal chains inequivalent, with the outer ones (Si_{ad}^1) lying 0.06 Å above the inner ones (Si_{ad}^2) while their lateral distance to the top row bridge site is 0.1 Å smaller for the formers. Both trends may be explained from the symmetry constrain on the top row silver atoms along the glide plane, as they cannot shift laterally, as well as by certain Ag-mediated repulsion between the Si_{ad}^2 in adjacent NRs (now each top silver atom makes two bonds with the Si_{ad}^2) that shifts the pentagonal rings away from each other by 0.2 Å. Concerning the substrate MR reconstruction there is a 0.1 Å lateral shift of the top row atoms away from the troughs in order to better accommodate the Si NRs. Finally we recall that the fact that the four Si_{ad} in the DNR are not colinear is a key factor in determining the aspect (arrangement of the protrusions) in the STM images.

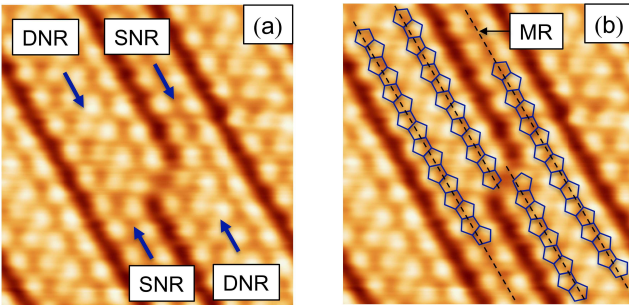


FIG. 7. **Dislocation defects between NRs.** (a) Experimental STM image showing a dislocation within the array of DNRs. The image size is $6.2 \times 6.2 \text{ nm}^2$. The sample bias voltage is 0.9 V and the tunnel current 0.8 nA. (b) Same as (a) after superimposing the Si pentagons (blue) and the MRs (dashed solid lines). The upper and lower truncated MRs at the center are shifted from each other by one Ag lattice parameter, leading to a DNR-SNR arrangement at the top of the image and a SNR-DNR at the bottom.

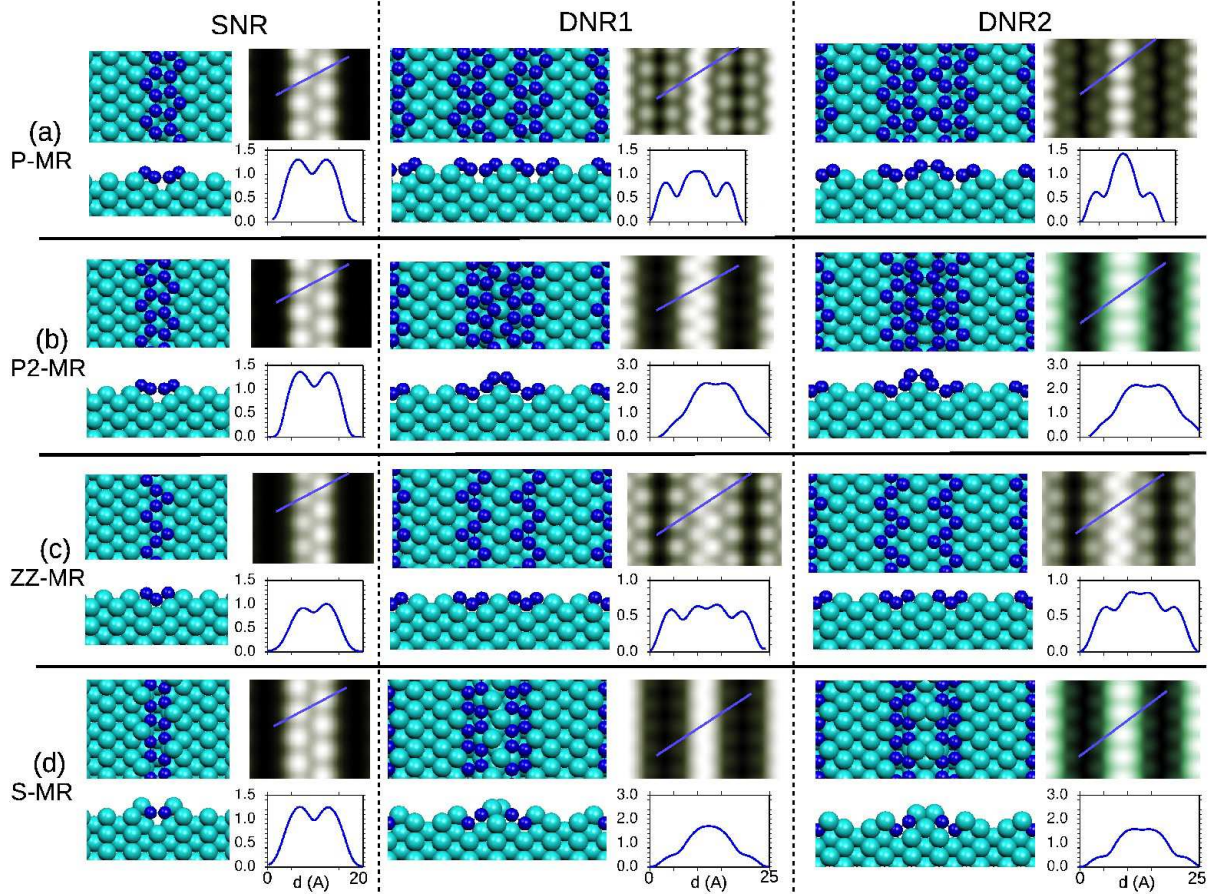


FIG. 8. **Trial MR-NR models:** Optimized geometries, STM topographic maps and line profiles for the most relevant MR-based NR structures considered in this work (we omit the tens of models tested based on an unreconstructed Ag(110) surface since they systematically relaxed towards geometries incompatible with the experimental STM images). Left panels correspond to the low coverage SNRs, and center and right columns to the high coverage DNR arrangements following a $-LL-RR-LL$ (DNR1) and a $-LR-RL-LR-$ (DNR2) sequence among the enantiomers, respectively. (a) P-MR model already shown in Figure 3 together with the alternative DNR2 arrangement whereby the Si_{ad} become aligned between the adjacent rings and dimerize on top of the short bridge sites leading to a broad ribbon made up of elongated octagons at the center decorated by pentagons at the edges. (b) P2-MR model similar to the P-MR one but with the Si_{ad} leaning towards top sites. (c) zig-zag missing row model (ZZ-MR) proposed in Ref. [12]. The motif in this pattern consists of only two Si_{s} atoms residing in the MR troughs, each of them bonded to another two Si_{ads} which lean towards the Ag atoms at the top row and protrude out of the surface. (d) a substitutional model (S-MR) where the extracted silver atoms attach to the Si_{s} located in the MR troughs (i.e. equivalent to the P-MR but with the Si_{ad} replaced by Ag_{ad}). Such model would be consistent with a site exchange mechanism between two Si and one silver top row atom without the need for diffusion of the latter across long distances over the surface. All SNRs yield STM images highly reminiscent of the experimental one (Fig. 1(b)), with the only exception of the ZZ-MR structure, which shows an asymmetry in the protrusions due to the lack of a glide plane. However, in both DNR arrangements for the P2-MR and S-MR models as well as in the P-MR DNR2 structure, the adatoms (Si_{ad} or Ag_{ad}) are raised above the silver top row by large distances in order to establish bonds among the adjacent NRs and the corresponding STM images deviate substantially from the high coverage experimental one (Fig. 1(c)) as their aspect is now dominated by these high lying Si/Ag atoms. Therefore, these structures may be discarded based on their STM topography. The ZZ-MR DNRs, on the other hand, present a nice correspondence with Fig. 1(c), specially the DNR2 arrangement which exhibits a glide plane symmetry. Anyhow, this model may be ruled out as well based on energetic arguments (see Table II and Fig. 9).

Model	SNR			DNR1 ($-LL - RR - LL$)			DNR2 ($-LR - RL - LR$)		
	$N_{Si/Ag}$	E_{ads}^{LDA}	E_{ads}^{GGA}	$N_{Si/Ag}$	E_{ads}^{LDA}	E_{ads}^{GGA}	$N_{Si/Ag}$	E_{ads}^{LDA}	E_{ads}^{GGA}
P-MR	6/88	6.44	5.70	12/86	6.43	5.70	12/86	6.40	6.57
P2-MR	6/88	6.24	5.56	12/86	6.23	5.68	12/86	6.41	5.49
ZZ-MR	4/88	6.36	5.59	8/86	6.35	5.58	8/86	6.34	5.58

TABLE II. **Si adsorption energies:** Adsorption energies per Si atom, in eV, obtained both under LDA and GGA according to eq. (1) for the different MR models considered (except the S-MR). They range between 6.2 – 6.4 for LDA and 5.5 – 5.7 eV for GGA. The large 0.7 eV difference between the two functionals is caused by their well known over- and under-binding nature, respectively. Nevertheless, both functionals point to the P-MR SNR and DNR as the most stable ones (marked in bold face in the table) the two attaining very similar values.

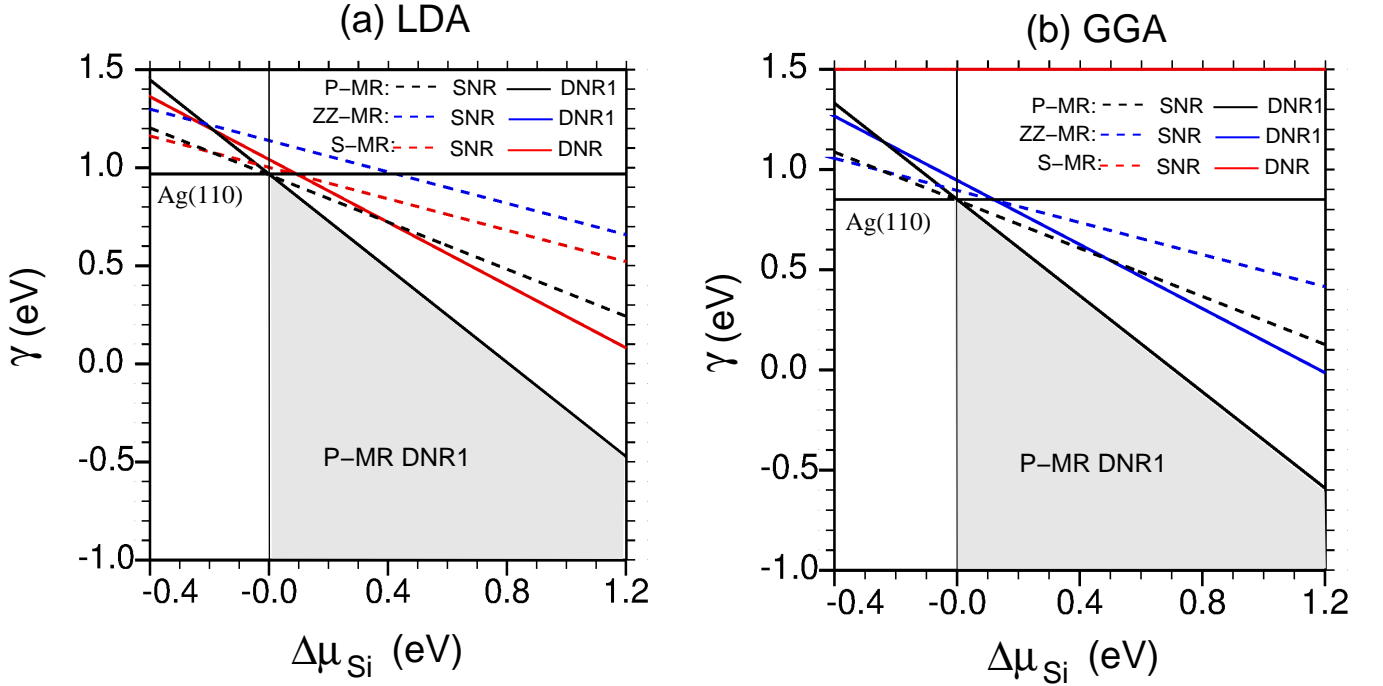


FIG. 9. **Stability of the NR trial models:** Phase diagram for the different Si-NR-Ag(110) models studied in this work under the (a) LDA and (b) GGA. Formation energies, normalized to the Ag(110)-(1 × 1) unit cell, are plotted as a function of the Si chemical potential μ_{Si} according to eq. (3). Note that among those structures with the same number of Si and Ag atoms, we only include the one with largest adsorption energy per Si atom (see Table II), since those omitted run parallel in the plot but shifted upwards. The origin for μ_{Si} has been placed at the first crossing with the formation energy of the clean Ag(110) surface (dark horizontal line) –see ‘Methods’ for further details. The shaded region indicates the most stable phase for $\Delta\mu_{Si} > 0$, which under both XC functionals corresponds to the P-MR DNR structure. The ZZ-MR and S-MR models, on the other hand, may be ruled out throughout the entire $\Delta\mu_{Si}$ range. Note that the P-MR SNRs start to become more stable for $\mu_{Si} < 0$ in qualitative agreement with the experimental observation, as SNRs are typically formed at small Si coverages, while the DNR phase tends to cover the entire surface as the coverage is increased.

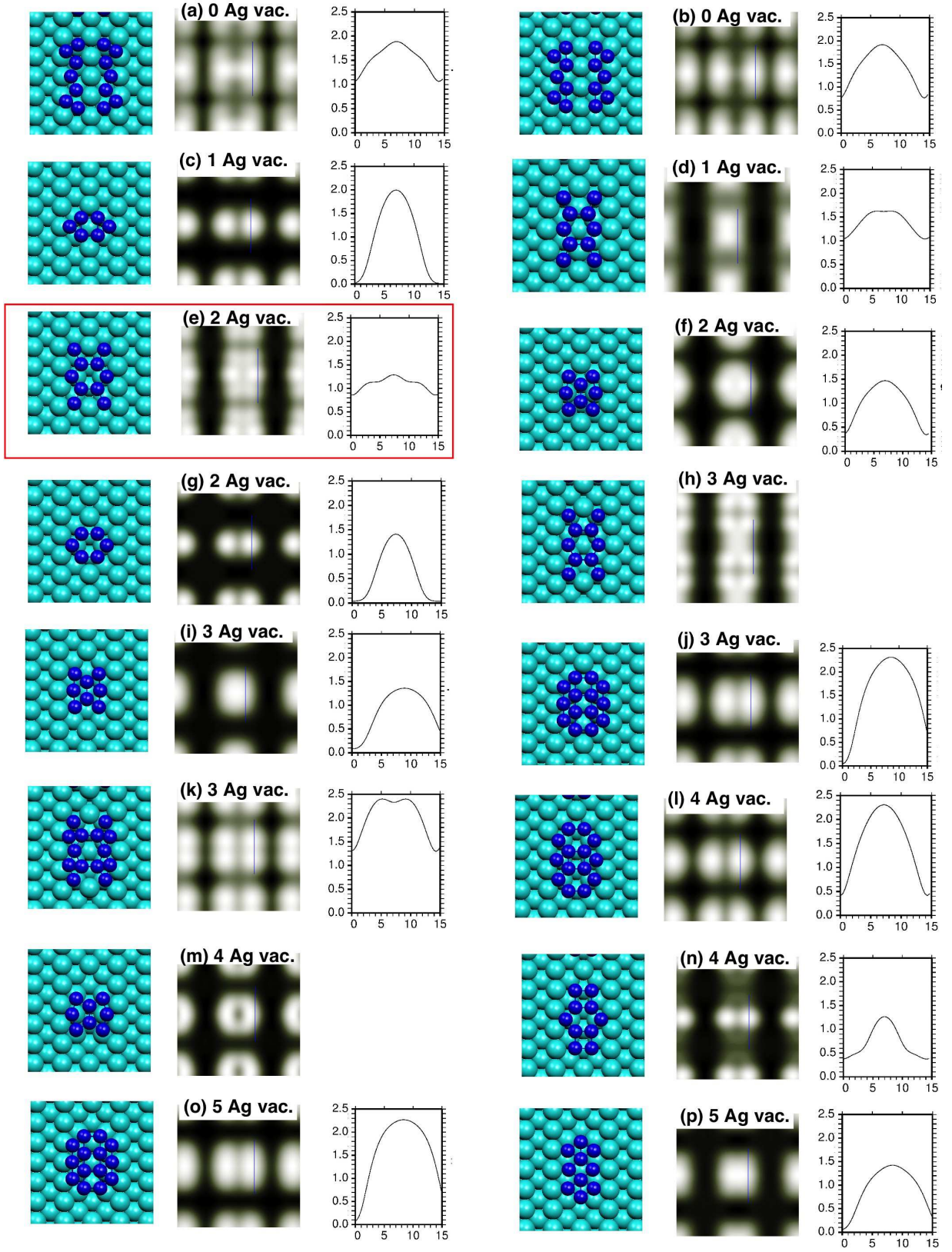


FIG. 10. **Trial nano-dot models:** Summary of the most relevant *nano-dot* trial structures studied in this work employing a reduced (4×5) or (4×6) supercell. Optimized geometries (top view), STM simulations and line profiles along the vertical blue lines shown in the maps for all *nano-dot* models tested. The models are organized from (a-p) with increasing number of silver vacancies, ranging from zero up to five. The structure that best matches the experimental image and line profile given in Fig. 2(a) is clearly case (d), involving two Ag vacancies and ten Si atoms. The simulated image correctly captures the two large bumps at the center and the dimmer maxima (elbows) above and below them. Furthermore, the associated profile is the only one that resolves the three maxima with just a few tenths of Angstrom difference between the center and the satellite ones, in perfect agreement with the experiment.